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DR. D. MILLS
Director of Research

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THE CHEMISTRY OF FOG WATER

Y.T. Tam
Atmospheric Physicist
Environmental Science Section

ABSTRACT

Fog frequently occurs for extended periods of time during freezing rain storms. Fog water can be intercepted by insulators and lead to icing and wetting. Contaminants in the fog water would thus be deposited on the insulators. This report contains a summary of the data on the chemistry of fog water as measured at Trafalgar TS and as reported in the open literature. The few measurements made at Trafalgar TS indicate that the conductivity of fog water is highly variable, exceeding 1000 $\mu\text{S}/\text{cm}$ on one occasion. Similar conclusions were drawn from the literature data. While these results suggest that fog water may be an effective medium for contaminating insulator surfaces, such conclusions must await the collection of additional field data. It is recommended that the study of fog water be expanded.

1.0 INTRODUCTION

The occurrence of insulator flashovers during freezing rain storms has become an important issue within Ontario Hydro. It is known that insulator flashovers require the existence of a conducting liquid film on the insulator surfaces. There are several ways of forming such conducting films on insulators: (1) freezing precipitation with ice or water bridging; (2) condensation on contaminated insulators; and (3) fog water accretion.

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An analysis by Schaedlich (1987) of the flashover events which occurred during 1969 to 1986 indicated that most of the events were accompanied by extended periods of fog. Some of these cases involved sub-zero temperatures when condensation would not have been expected. One event, on March 10, 1986, involved long periods of sub-zero temperature, fog, light freezing precipitation and rising temperatures towards the end of the event. This event caused 58 flashovers, 27 of them on transmission line insulators in an area just west of Toronto.

These incidents led to the initiation of a number of research studies. One of these involved the measurement of the microphysical, meteorological and chemical properties of freezing rain storms. As part of this study, a storm, in many ways similar to the March 10, 1986 one, was observed on March 12, 1988 (Tam, 1988). The one major difference between the two storms was the absence of fog (and flashovers) in the more recent event. From the data available, however, it was not possible to determine what the role of fog is - to maintain the air saturated during the period of slowly rising temperatures so that condensation can occur, or to ice/wet and contaminate the insulators by the wet growth of ice from super-cooled fog.

The phenomenon of fog has been studied for many years. Most of the early studies dealt with fog formation and its effect on visibility. However, some attention has been given to the chemistry of fog in recent years. Unfortunately, most of the fog water chemistry data refer to mountainous and/or coastal areas. There are no data for the Southern Ontario region.

Accordingly, an effort was made to measure the chemistry of fog water in Southern Ontario, as part of the study mentioned above. The field study was carried out at an instrumented station located at Ontario Hydro's Trafalgar Transformer Station (see Figure 1). This report summarizes data on the chemistry of fog water, based on some samples collected during the field study and from a search of the open literature.

2.0 APPROACH

The fog water samples were collected in the field by means of a passive fog water collector. As shown in Figures 2 and 3, the collector is constructed of polyethylene with Teflon strings. There are about 370 strings of 45-cm length and 0.53-mm diameter spaced 3 mm apart in two concentric circles. The fog water droplets that impact on the strings run down into a funnel and then into a collection bottle. Collection rates are dependent on wind speed and generally are in the range of a few mL to a few 100's mL an hour.

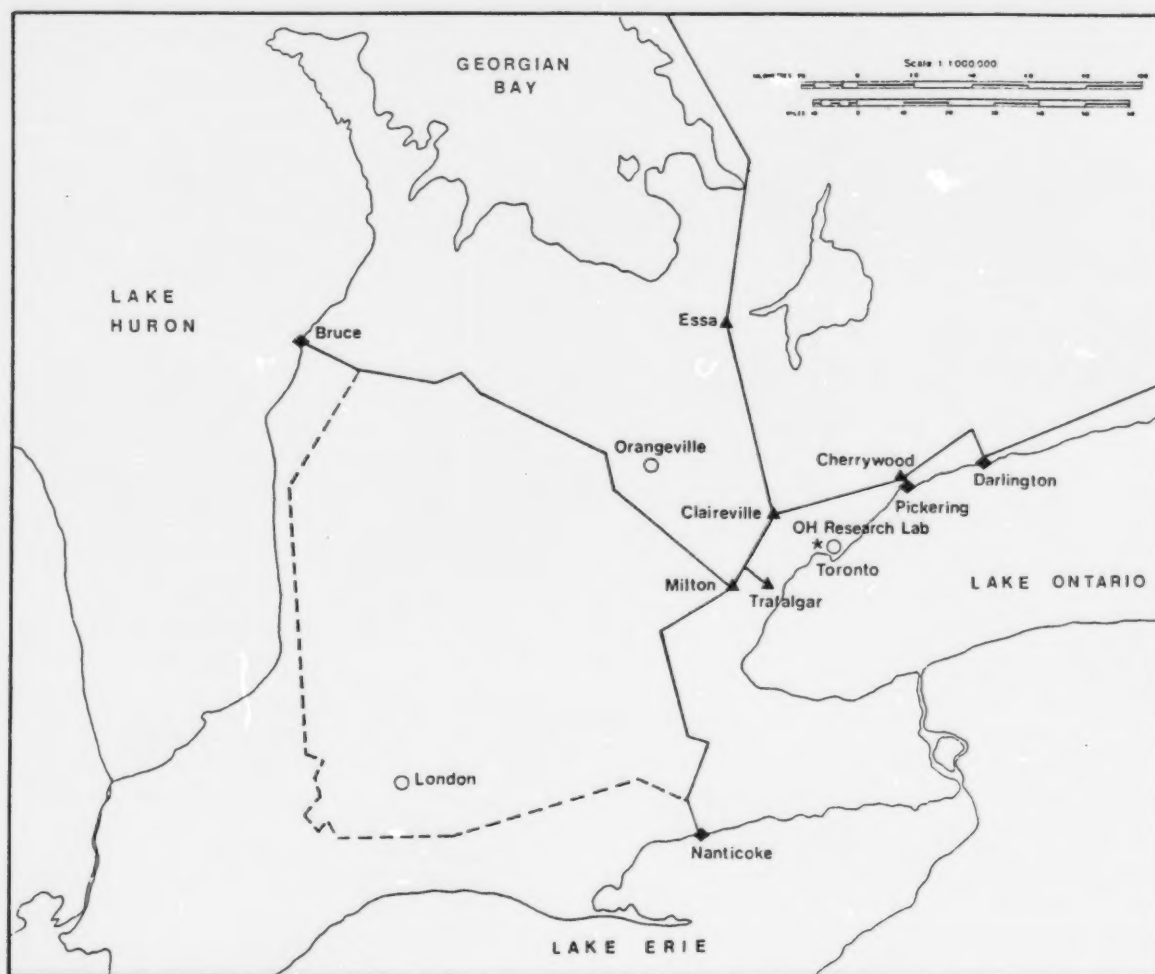


FIGURE 1
 LOCATION OF THE 1987-1988 FIELD
 STUDY OF FREEZING PRECIPITATION AND FOG EVENTS

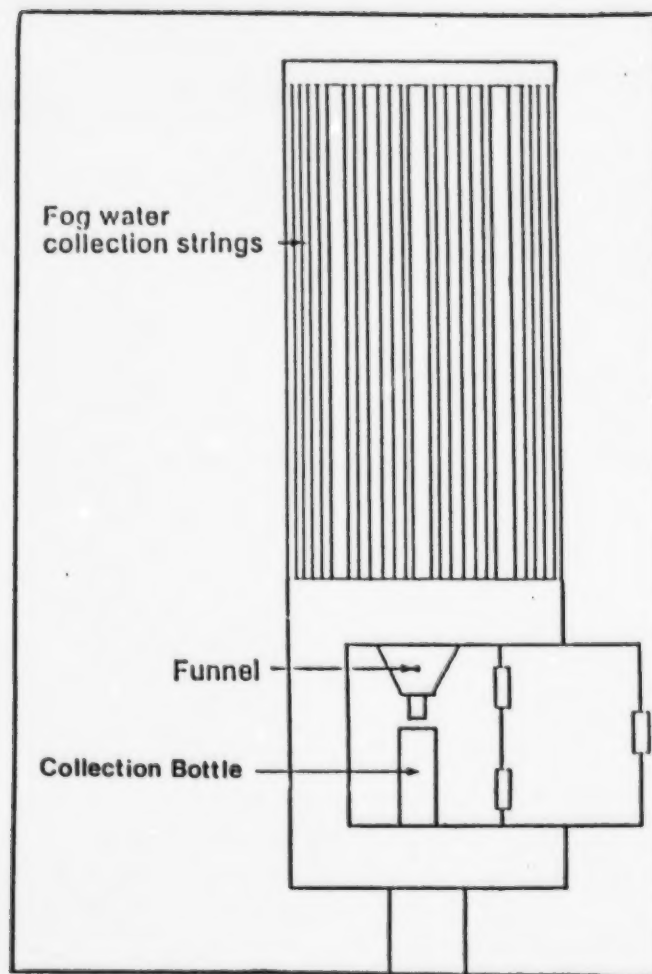


FIGURE 2
THE PASSIVE FOG WATER COLLECTOR

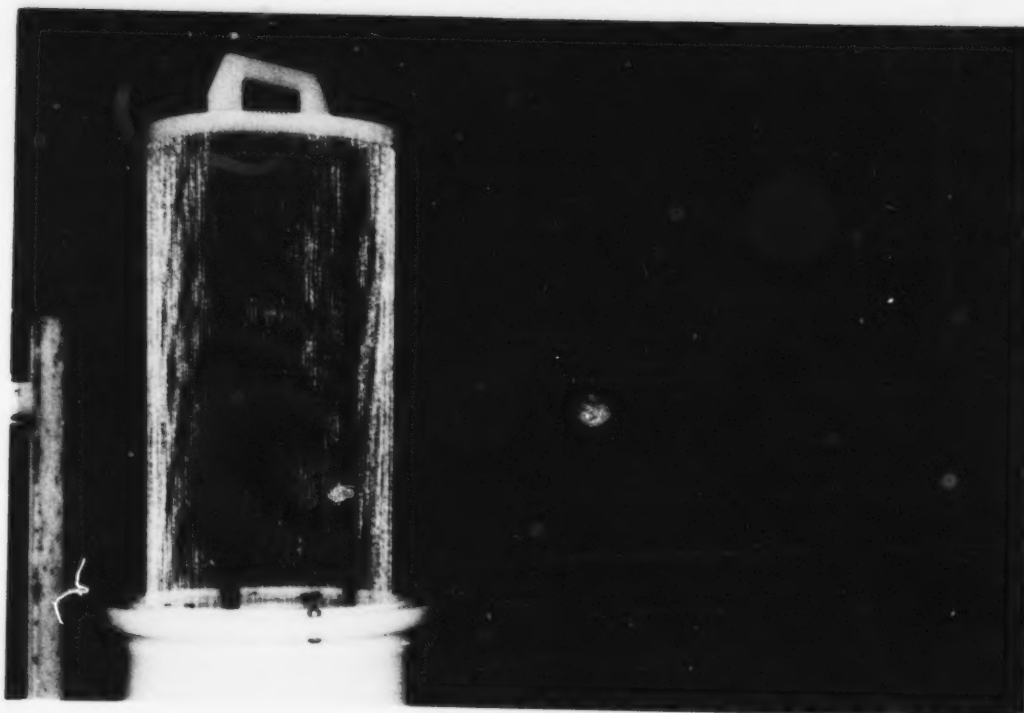


FIGURE 3

A VIEW OF THE FOG WATER COLLECTOR AT THE
TRAFALGAR SITE DURING A FOG EVENT

To ensure the accuracy and precision of the measurements, the collector was thoroughly cleaned with deionized water before exposure. Contamination from blowing dust was minimal. The ground at the Trafalgar field station is flat and covered with gravel. During most of the Winter it was frozen and intermittently covered with snow.

The sampler was operated on an event basis. When an event was identified, the collector was placed on a platform at about 1 m above ground. As soon as the fog event was seen to have stopped, the sample was removed, sealed, and refrigerated at the site. The sample was then transported to the laboratory where pH, conductivity and major ion concentrations were measured, using standard analytical techniques.

Since the collection efficiency of the passive fog water collector is wind speed dependent, its collection rate declines significantly under calm or low wind conditions. To improve this situation, an air fan was placed downwind of the collector to draw the fog water-laden air through the collector. The collection efficiency of the device when operated with the air fan needs to be tested.

When reviewing the literature dealing with the chemistry of fog water, it was observed that the conductivity was not always measured. As a result, we've had to estimate it from the reported ionic composition. By definition, the conductivity is the conductance per unit cube of solution where the conductance of a solution is the reciprocal of the resistance. It may be determined as the sum of the contributions from the movement of each kind of ion present. Thus, a general formula for calculating conductivity (in $\mu\text{S}/\text{cm}$) may be expressed as:

$$\text{COND} = 10^{-6} \sum_i C_i Z_i X_i \quad (1)$$

where C_i is the molar concentration of the i th ion with charge Z_i and X_i is the equivalent conductivity of the ion (in infinitely dilute solutions). The major ions in condensed water in the atmosphere are hydrogen, H^+ , sulfate, SO_4^{2-} , nitrate, NO_3^- , ammonium, NH_4^+ , chloride, Cl^- , sodium, Na^+ , calcium, Ca^{2+} , magnesium, Mg^{2+} , and potassium, K^+ . Using the equivalent conductivity of these ions from the CRC Handbook of Chemistry and Physics, 54th edition, Equation (1) may be written as

$$\begin{aligned} \text{COND} = & 0.350[\text{H}^+] + 0.158[\text{SO}_4^{2-}] + 0.0706[\text{NO}_3^-] \\ & + 0.0745[\text{NH}_4^+] + 0.0755[\text{Cl}^-] + 0.0509[\text{Na}^+] \\ & + 0.120[\text{Ca}^{2+}] + 0.106[\text{Mg}^{2+}] + 0.0745[\text{K}^+]. \end{aligned} \quad (2)$$

Here, ion concentrations are expressed in $\mu\text{moles/L}$. Since the conductivity is highly dependent on the sample temperature, see Figure 4, the value calculated by Equation (2) refers to a temperature of 25°C. At 0°C the conductivity would be about 60% of the value at 25°C.

3.0 RESULTS AND DISCUSSION

A total of nine fog water samples were collected at the Trafalgar site during the 1987-88 winter field study. These samples included fog water and fog water mixed with some precipitation that entered the collector during the sampling period. Table I gives the date, the pH, conductivity and sample type for each of these nine samples.

The conductivity of fog water was in the range of 86 to 1,007 $\mu\text{S/cm}$, with an average of 381 $\mu\text{S/cm}$. This is to be compared to values of 31 to 67 $\mu\text{S/cm}$, with an average of 48.6 $\mu\text{S/cm}$, for the fog mixed with precipitation samples. The overall average of these nine samples is 196.3 $\mu\text{S/cm}$. Table I also gives the conductivity of the precipitation collected during the same sampling dates. The average conductivity of the coincident precipitation samples was 48.5 $\mu\text{S/cm}$. Thus, fog water has a much higher conductivity than fog water mixed with precipitation or precipitation alone.

The pH of fog water was in the range of 2.9 to 4.6, whereas the pH of fog water mixed with precipitation was in the range of 4.1 to 5.4. The overall average pH of the nine samples is 4.29. The pH of the coincident precipitation samples was in the range of 3.9 to 5.4, with an average of 4.5, which is higher than the overall average pH for fog water and fog water mixed with precipitation.

The chemical compositions of the fog water and some coincident precipitation samples are given in Table II. In general, the concentrations of all chemical species were higher in fog water than in precipitation. Sulfate and nitrate were the major anions and ammonium and calcium were the dominant cations.

The conductivities of the collected fog water and precipitation samples were further calculated using Equation (2) and the concentrations of chemical species. The measured and calculated results are shown in Figure 5. At the low end, the scatter around the 1:1 line is to be expected given the accuracy of the individual concentration measurements used in the calculation of conductivity. The deviation at the high end appears to indicate that not all ions have been analyzed for.

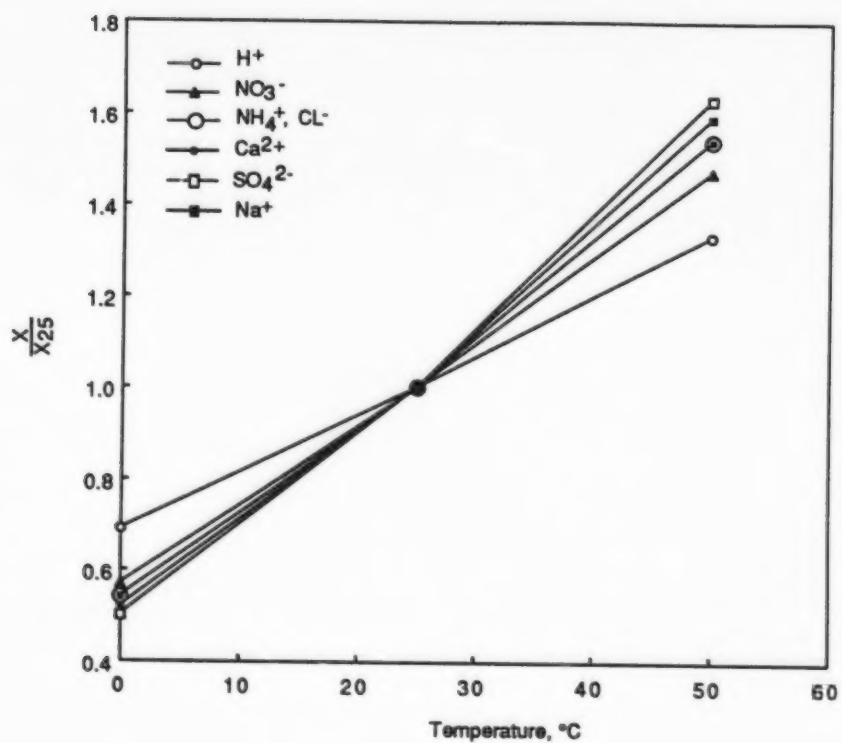


FIGURE 4
THE EFFECT OF TEMPERATURE ON THE
EQUIVALENT CONDUCTIVITY, X, OF
SEVERAL IONS

TABLE I
THE pH AND CONDUCTIVITY OF FOG WATER
COLLECTED AT THE TRAFALGAR SITE

(values in brackets represent those of rain/snow)

Date	pH	Conductivity (μ S/cm)	Sample composition
Nov 19, 1987	4.6	86	fog
Nov 29, 1987	4.1 (4.1)	67 (43)	fog + rain
Dec 20, 1987	4.4 (4.2)	31 (31)	fog + rain
Jan 19, 1988	4.1 (4.3)	47 (34)	fog + snow
Mar 28, 1988	5.4 (5.4)	41 (33)	fog + rain
Apr 2, 1988	2.9	1007	fog
Apr 2, 1988	3.4 (3.9)	308 (97)	fog
Apr 3, 1988	5.3 (4.5)	57 (30)	fog + rain
Apr 7, 1988	4.4 (4.1)	123 (73)	fog

TABLE II
THE CHEMICAL COMPOSITION OF FOG WATER
COLLECTED AT TRAFALGAR SITE (μ moles/L)

(values in brackets represent those of rain/snow)

Chemical Composition	Nov 19 1987	Nov 29 1987	Dec 20 1987	Jan 19 1988	Mar 28 1988
Sulfate (SO_4^{2-})	168	82 (266)	39 (26)	45	51
Nitrate (NO_3^-)	125	105 (55)	50 (47)	76	96
Chloride (Cl^-)	107	23 (31)	6 (54)	18	31
Ammonium (NH_4^+)	95	101 (16)	37 (22)	49	77
Sodium (Na^+)	104	14 (2)	7 (3)	13	30
Calcium (Ca^{2+})	157	49 (4)	20 (4)	22	47
Magnesium (Mg^{2+})	146	9 (1)	6 (2)	7	14
Potassium (K^+)	9	5 (1)	2 (1)	2	2
pH	4.6	4.1 (4.1)	4.4 (4.2)	4.1	5.4
Hydrogen* (H^+)	25	79 (80)	40 (63)	80	4
Cond (measured)	86	67 (43)	31 (31)	47	41

* determined by the pH value

TABLE II (cont'd)

Chemical Composition	Apr 2 1988(am)	Apr 2 1988(pm)	Apr 3 1988	Apr 7 1988
Sulfate (SO_4^{2-})	424	214 (80)	200 (31)	194
Nitrate (NO_3^-)	277	481 (95)	138 (26)	303
Chloride (Cl^-)	451	108 (20)	29 (3)	51
Ammonium (NH_4^+)	555	183 (32)	93 (17)	257
Sodium (Na^+)	15	32 (17)	14 (4)	39
Calcium (Ca^{2+})	64	88 (14)	147 (8)	167
Magnesium (Mg^{2+})	20	28 (6)	16 (2)	32
Potassium (K^+)	5	5 (2)	14 (1)	8
pH	2.9	3.4 (3.9)	5.3 (4.5)	4.4
Hydrogen* (H^+)	1259	355 (129)	5 (33)	40
Cond (measured)	1007	308 (97)	57 (30)	123

* determined by the pH value

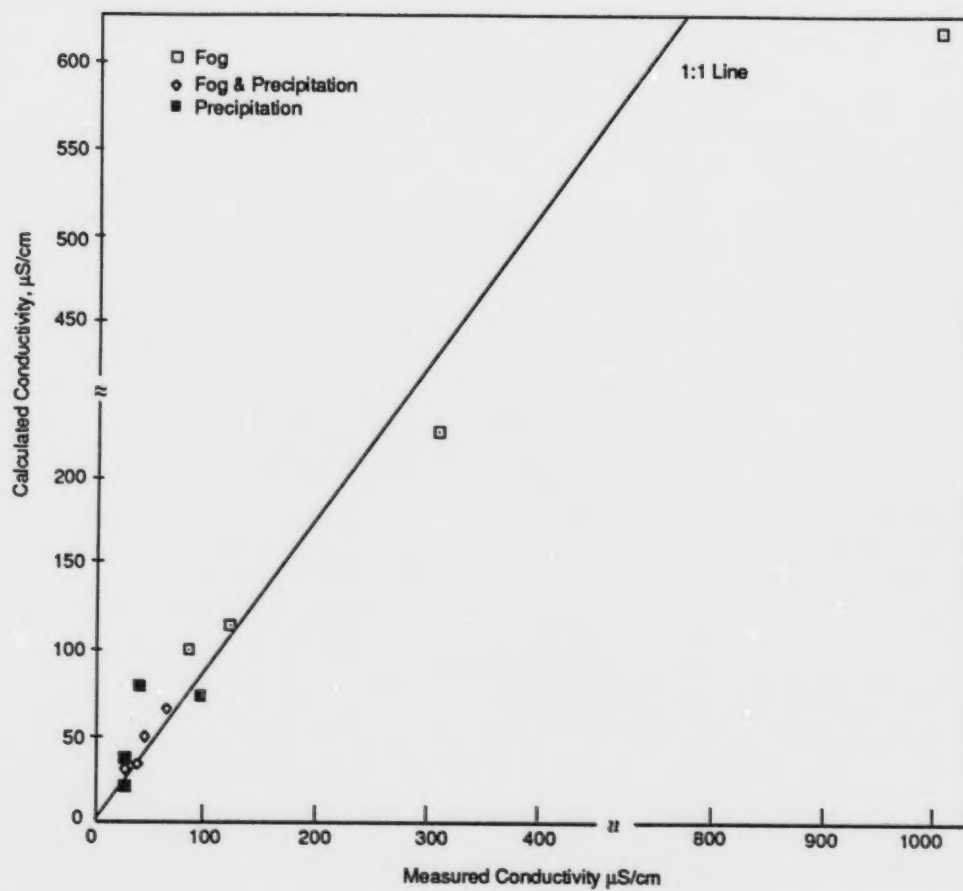


FIGURE 5
COMPARISON OF MEASURED AND
CALCULATED CONDUCTIVITIES

Table III gives a summary of the fog water chemical composition data reported in the open literature. These cases were chosen mainly for the completeness of the chemical analysis and the fact that the three major types of fog water are represented: mountainous, coastal and urban fogs. The fog water samples summarized in the table were collected from coast-to-coast in North America and in Italy and Germany. The earliest samples were collected in the 1930's, but most of the studies were carried out in the early 1980's. Except for the earliest ones, almost all the important ions were included in the analysis.

The pH values of the mountainous fogs were in the range of 3.5 to 4.3, with an average of 3.63. Sulfate and nitrate were the dominant anions with a ratio of sulfate to nitrate of about 1.5. Hydrogen and ammonium were the dominant cations. The measured conductivities of fog water at the Allegheny Mountain and Mt. Tremblant were 159 and 129 $\mu\text{S}/\text{cm}$, respectively. Those calculated by Equation (2) were in the range of 41 to 313 $\mu\text{S}/\text{cm}$. The overall average conductivity of these mountainous fogs is 109.7 $\mu\text{S}/\text{cm}$.

The coastal fogs had pH values in the range of 2.2 to 6.3, with an average of 3.98. All but two samples had pH values <5.0 and 70% of the total samples had pH values <4.0 . Again, the dominant anions were sulfate and nitrate and the dominant cations were hydrogen and ammonium. Concentrations were much higher than in the mountainous fogs. Further, there were very high concentrations of sodium and chloride observed in the coastal fog samples. This is attributable to sea salt nuclei. The calculated conductivities of the coastal fogs were between 35 and 4,300 $\mu\text{S}/\text{cm}$, with an average of 757.4 $\mu\text{S}/\text{cm}$.

The pH values of the urban fogs were between 2.6 and 7.1. The distribution of ion concentrations was relatively uniform with sulfate, nitrate and ammonium being the dominant ions. The measured fog water conductivity in Los Angeles, California was in the range of 260 to 1,190 $\mu\text{S}/\text{cm}$. The calculated fog water conductivities in Albany, New York and Indianapolis, Indiana were in the range of 68 to 564 $\mu\text{S}/\text{cm}$. The overall average pH and conductivity of these urban fogs is 3.97 and 353.6 $\mu\text{S}/\text{cm}$, respectively.

A regional summary of the fog water pH and conductivity is given in Figure 6. Both the pH and conductivity varied between and within regions. The lowest pH values were observed in Southern California (2.7) and in Southern Ontario (2.9). The highest fog water conductivities were also measured in Southern California (1,190 $\mu\text{S}/\text{cm}$) and in Southern Ontario (1,007 $\mu\text{S}/\text{cm}$). It is apparent that the conductivity of fog water is quite variable, reaching values in excess of 1000 $\mu\text{S}/\text{cm}$ on occasion. However, more data are required before any conclusive generalizations can be drawn.

TABLE III

A SUMMARY OF FOG WATER CHEMICAL COMPOSITION
($\mu\text{eq/L}$), PH AND CONDUCTIVITY ($\mu\text{S/cm}$)
COLLECTED AT SOME DIFFERENT LOCATIONS

LOCATION	pH	H ⁺	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Cond	Ref
MOUNTAINOUS FOG ITALY												
Po Valley Feb 1984	3.5- 4.3		400- 900	290- 1100	20- 120	580- 1620	10- 110	60- 130	10- 50		138- 313*	3
NEW YORK Whiteface Mt Aug 1976	3.7		140	90	31	89	11	17	6		41*	2
Aug 1980	3.2- 4.0	63- 630	32- 800	7- 190	1- 14	4- 310	1- 55			1-6	190- 224*	2
PENNSYLVANIA Allegheny Mt Aug 1983	3.5	340	387	230	26	144	155	1			159	12
QUEBEC Mt Tremblant Summer 1986	3.7		258	198	12	243	9	29	17	1	129	14
COASTAL FOG GERMANY												
Baltic Sea 1955-1965	3.8		1860	900	1740	2335	1500	750		240	848*	9
Dresden 1955-1965	4.2		3300	380	585	2100		3180			1132*	9
MAINE Brooklin 1930-1940	3.5- 6.3		95- 770		0-140						129*	5
CALIFORNIA												
Central Coast Fall 1976			200- 70-490	115- 24-235	400- 95-1240	190- 0-580	320- 80-950	55- 9-100	68 23-175		114*	11
Corona del Mar Dec 7, 1982	2.2	6920	1290	7900	1050	2860	725	197	188	71	4290*	7
Del Mar Jan 9, 1983	2.9	1410	469	1850	614	781	511	49	130	9	850*	7
Long Beach Jan 6, 1983	4.9	13	487	252	221	759	62	45	26	12	185*	7
Lennox Dec 7, 1981	3.0	1100	926	2210	178	1610	65	111	42	12	844*	7
Jan 6, 1983	3.6	237	126	365	68	464	41	39	18	8	177*	7
Morro Bay July 14, 1982	6.2		214	114	1200	107	746	120	221	64	222*	7
Mt. Sutro Aug 13, 1982	4.0	102	319	87	851	183	648	93	170	52	237*	7
Pt. Reyes Aug 9, 1982	4.5		186	23	215	64	190	10	36		67	7
San Nicholas Is. Aug 26/83	3.5-5.0		54-1280	6-526	57-4580	43-327	42-3520	3-242	10-890			
San Marcos Pass. Aug 20 1983	3.9	138	2080	1580	5490	452	6060	450	1500	148	1473*	7
NOVA SCOTIA Aug 1975	4.5	32	55	74	19	97	10	3	4	3	35*	7
URBAN FOG NEW YORK Albany Oct 1982	5.8 4.3-6.4		155	85 21-1360	47 11-220	215 18-175	36 70-350	120 10-100	13 65-350		68*	4
INDIANA Indianapolis												
Dec 9, 1985	3.1	794	731	943	68	676	26	100	37	11	468*	10
Jan 23, 1986	3.8	174	1240	1000	140	1300	108	808	226	19	564*	10
Feb 18, 1986	3.8	166	589	344	185	787	32	31	3	5	180*	10
CALIFORNIA												
Pasadena Nov 15, 1981	4.7- 5.3	5.6- 55	62- 380	130- 930	56- 280		12- 496	19- 360	7- 153	4- 39	56- 281*	11
Dec 20, 1981	3.8	178	450	1000	161	1773	51	217	89	373	412*	11
Los Angeles Fall 1980	3.3 2.7-7.1	479 0-2000	292 177-938	1110 580-2980	223 68-423	1580 420-4260	139 30-620	84 0-230	27 11-165	24 8-220	398 257-1190	1
Bakersfield Jan. 1983	4.2 2.6-7.0	60 0-2750	1160 194-9400	850 200-6800	47 1-980	1440 490-13300	20 1-325	47 7-3500	6 1-430	9 2-368	385*	6

*Denotes the calculated values

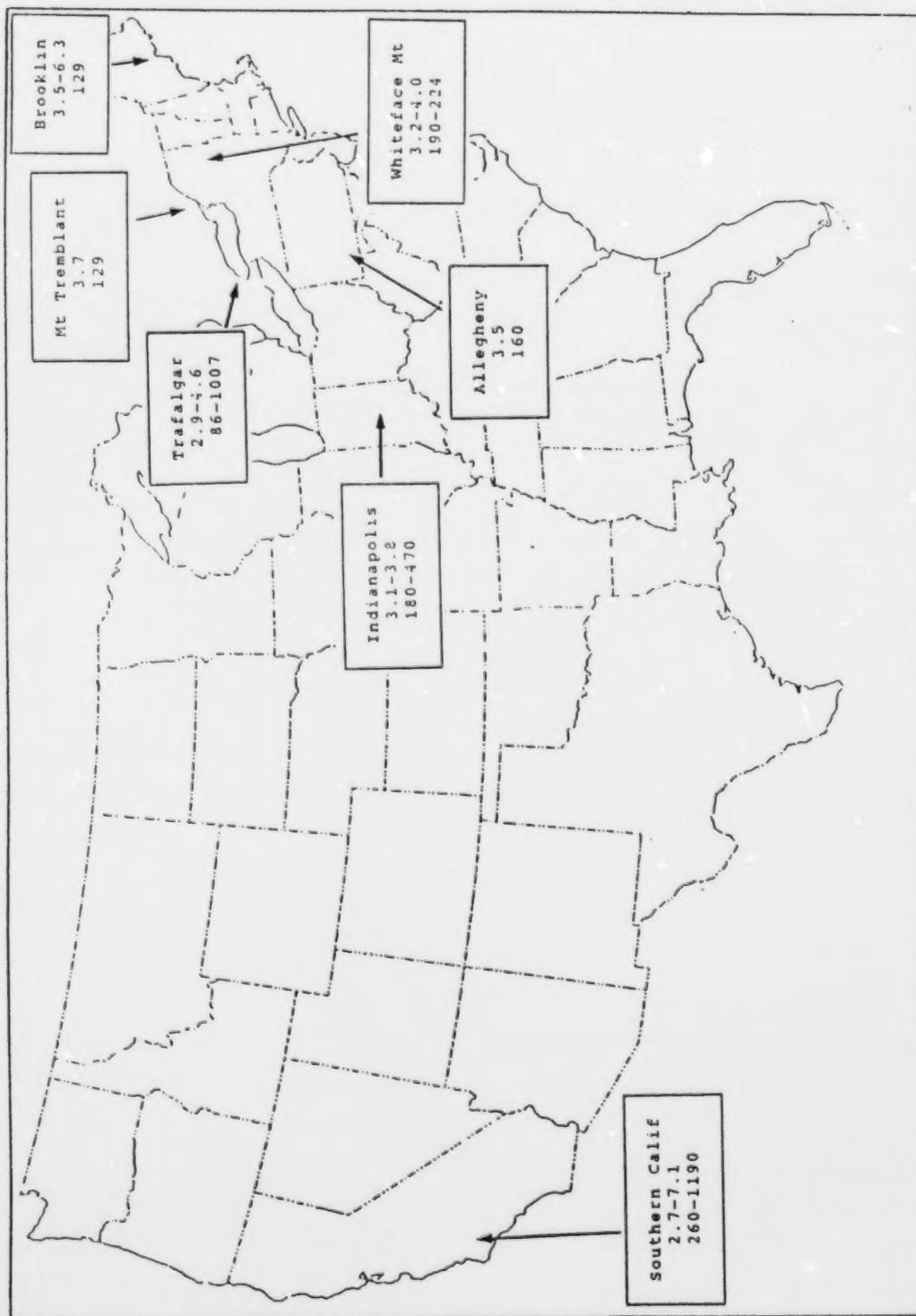


FIGURE 6

A REGIONAL SUMMARY OF FOG WATER PH AND CONDUCTIVITY IN $\mu\text{S}/\text{cm}$

4.0 CONCLUDING REMARKS

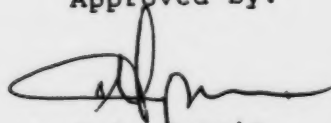
The purpose of this report was to present a summary of the chemistry of fog water, based on the Trafalgar field measurements and the data reported in the literature. Our fog water samples were collected in the field with a passive collector which was operated from the beginning to the end of an identified event. Samples were analyzed in the laboratory for pH, conductivity and major ions.

Results from the field measurements at Trafalgar indicated that all fog samples are acidic. There was a large variation in pH values, with the lowest values being 2.9 and the highest 5.4. The conductivity of fog water was quite variable, reaching a value in excess of 1000 $\mu\text{S}/\text{cm}$ on one occasion.

Of all the events abstracted from the literature, 82% had pH values <5.0 and 57% had pH values <4.0 . The conductivity of these events ranged from 35 to 4,300 $\mu\text{S}/\text{cm}$. Conductivity is generally higher on the west coast than on the east coast. The dominant anions were sulfate and nitrate while the dominant cations were hydrogen and ammonium. The concentrations of sodium and chloride are very high in some samples collected in coastal regions.

In summary, some fog water chemistry data have been gathered in our field measurement studies and from the open literature. These data confirm that fog water is more acidic and has a higher conductivity than precipitation. While these results suggest that fog water may be an effective medium for contaminating insulator surfaces (cf, Melo, 1988), such conclusions must await the collection of additional field data. It is recommended that the field study of fog liquid water content and ionic composition be expanded.

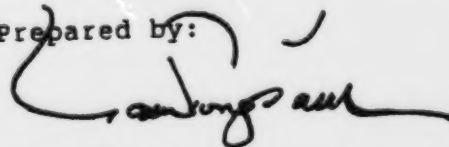
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Manager
Chemical Research Department

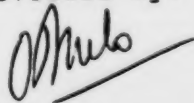
YTT/mf

Prepared by:



Y.T. Tam
Atmospheric Physicist
Environmental Science Section

Reviewed by:



O.T. Melo
Supervising Engineer
Environmental Science Section

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